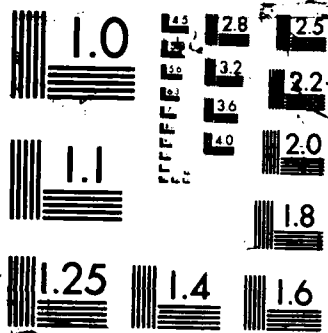


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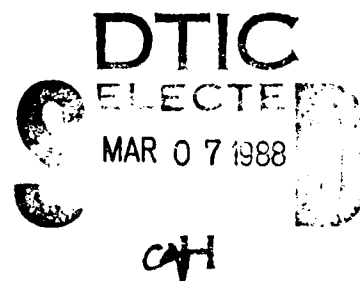
The Formation of Adsorbed O^{2-} and OH^-
on a Ag Electrode in Dilute CrO_4^{2-} Electrolytes

by

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The Formation of Adsorbed O^{2-} and OH^-
on a Ag Electrode in Dilute $\text{CrO}_4^{=}$ Electrolytes

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ABSTRACT

Surface enhanced Raman scattering has been used to detect *in situ* the formation of $O^=$ and OH^- adsorbed on a Ag electrode in an aqueous solution of $25\mu M Na_2Cr_2O_7$ and 10^{-2} to $10^{-3} M KCl$. Both oxide and hydroxide adsorbates are observed after completion of an oxidation-reduction cycle in a standard voltammetry experiment. As the Ag electrode voltage is swept cathodically, the O_{ads}^- is protonated to form more OH_{ads}^- but, unlike in MnO_4^- solutions, no further protonation to form H_2O occurs at any cell voltage. The addition of O_2 gas to the electrolyte deprotonates the adsorbed OH^- to form an oxide covered surface. These results for CrO_4^- solutions are contrasted with previous results for MnO_4^- electrolytes to obtain information about the nature of the metal-solution interface in chromate passivated metal surfaces.



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INTRODUCTION

Understanding the interactions of oxide covered metal surfaces with their environments is fundamental to understanding corrosion processes.¹ Only recently have *in situ* spectroscopic techniques been available to probe the detailed processes occurring in these systems as functions of concentration, pH, and electrochemical potential. Surface Enhanced Raman Scattering (SERS), sensitive to less than monolayer coverage of adsorbates on selected metal surfaces², is one technique that has become widely used. Due to recent developments in detector instrumentation, SERS is a very effective tool for investigating electrode processes during cyclic voltammetry.³

We are interested in the nature of the protonation processes of the oxide layer on Ag electrodes.⁴ Electrolytic solutions containing dilute concentrations of alkali or alkaline earth halides and the tetrahedral oxyanions PO_4^{-3} , VO_4^{-3} , or MnO_4^- have been studied. Each solution has a different effect on the Ag metal-electrolyte interface. Both PO_4^{-3} and VO_4^{-3} adsorb without decomposition and are protonated sequentially to form the adsorbed acids $\text{H}_n\text{XO}_4^{-(3-n)}$ as the electrode voltage, V_{SCE} , is swept cathodically (more negatively) relative to a saturated calomel electrode. However, there are differences in the adsorption properties of $\text{H}_n\text{PO}_4^{-(3-n)}$ and $\text{H}_n\text{VO}_4^{-(3-n)}$ on Ag metal. $\text{H}_n\text{VO}_4^{-(3-n)}$ remains contact adsorbed regardless of V_{SCE} and, therefore, interfacial pH.^{4c} At very negative V_{SCE} , the vanadium ion is reduced, but remains adsorbed even if H_2 is produced. $\text{H}_n\text{PO}_4^{-(3-n)}$ forms H_3PO_4 , which then desorbs, when the interfacial pH is brought below 4 by applying a negative V_{SCE} to the Ag electrode. ^{4d}

Solutions with micromolar concentrations of MnO_4^- behave quite differently.^{4a,b} After the Ag electrode has gone through an oxidation reduction cycle (ORC), a SERS peak, assigned to the Ag metal-oxide stretching mode, is observed at $\sim 600\text{ cm}^{-1}$. As V_{SCE} is swept cathodically, the oxide layer is protonated to form adsorbed OH^- ($\sim 500\text{ cm}^{-1}$) and, at very low interfacial pH, adsorbed H_2O ($\sim 400\text{ cm}^{-1}$). The formation of adsorbed H_2O is

confirmed by the appearance of a strong peak due to the O—H stretching mode at ~ 3500 cm^{-1} .

The addition of O_2 gas to an electrolyte with 10^{-5}M MnO_4^- and 10^{-3}M KCl has the remarkable effect of deprotonating the adsorbate layer stepwise to form the oxide layer. This reversible process is the result of the increased interfacial pH due to the reduction of dissolved O_2 .

In this paper, we report the SERS spectrum obtained from a Ag electrode in a 10^{-2} to 10^{-3}M KCl electrolyte containing $25\text{ }\mu\text{M}$ Na_2CrO_4 . The spectrum observed shows the formation of an oxide layer which is partially protonated to form adsorbed OH^- . Unlike the spectra from MnO_4^- solutions, no evidence of additional protonation of the adsorbed OH^- was seen. These results indicate that a significant factor in the passivation of metals by treatment with chromate solutions is the inability of the treated metal to form SERS active sites with adsorbed H_2O molecules.⁵

EXPERIMENTAL

A polycrystalline Ag electrode, polished with 0.5μ alumina and washed with double distilled H_2O , a Pt counter electrode, and a saturated calomel electrode (SCE) were placed in the electrolytic solution in a fused quartz optical cell. Standard methods of voltammetry were used to oxidize and reduce the Ag electrode surface.⁶ The voltage between the Ag electrode and the SCE was ramped linearly at 5mV/s . Distilled H_2O or commercial D_2O and reagent grade chemicals were used to prepare all solutions. The pH of the electrolyte was monitored before and after the experiment and ranged from 4.6 to 6.3. The concentration of the $\text{Na}_2\text{Cr}_2\text{O}_7$ was maintained at $25\text{ }\mu\text{M}$, a value chosen to minimize the absorption of the laser beam and to assure a solution containing predominately the HCrO_4^- ion.⁷

The Raman spectra were measured with an Ar ion laser operated at 514.5 or 488.0nm at an incident power of 100 mW focused to 1 mm^2 at the working electrode. The scattered

light, collected with an f1.2 lens, was focused on the entrance slit of a triple spectrograph. The dispersed light was detected with an optical multichannel linear diode array with a resolution of 2.5cm^{-1} per diode. The data were collected and massaged using a Microvax computer.

RESULTS

Figure 1 shows the time and voltage evolution of the SERS spectra from a Ag electrode in a 10^{-2}M KCl solution in D_2O containing $25\mu\text{M}$ $\text{Na}_2\text{Cr}_2\text{O}_7$ at a pD 6.3. The initial spectral frame is recorded at $-0.1 V_{SCE}$ as a second ORC linear voltage scan begins. As V_{SCE} sweeps to a positive voltage, the Ag electrode is oxidized forming an adherent layer of AgCl and Ag_2CrO_4 and resulting in the loss of nearly all the SERS intensity. Upon reduction during the subsequent cathodic sweep, a roughened Ag surface is formed containing adsorbed Cr ions and Cl^- . SIMS measurements on electrodes that had undergone similar treatment indicate that the Cr concentration is 1-2% of the total metal surface.⁹ A strong, broad, almost resolved SERS peak appears at $\sim 590\text{ cm}^{-1}$ after the faradaic reduction has ceased at $-0.05V_{SCE}$. During the cathodic sweep, the peak becomes broader and more intense, reaching a maximum intensity at $\sim -0.8V_{SCE}$. Just prior to the onset of D_2 gas formation, the peak becomes narrow. A distinct shoulder is observed at 642 cm^{-1} on a strong peak at 567 cm^{-1} . The intensity of both peaks diminishes as D_2 gas is formed. Upon switching to an anodic sweep at $-1.53 V_{SCE}$, the peaks become more resolved as the higher energy peak increases in intensity and the lower frequency peak decreases in intensity. A third ORC causes the reappearance of the original broad SERS peak.

No other spectral feature is observed except a small peak at 240 cm^{-1} which occurs at the end of each ORC and disappears during the cathodic sweep. This frequency shift and voltage behavior is characteristic of the stretching mode of Ag-Cl. The absence of a strong SERS peak at $\sim 850\text{ cm}^{-1}$, due to the symmetric stretching mode of CrO_4^{2-} , indicates that no adsorbed CrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$ exists. Previous results have shown that CrO_4^- adsorbs

on Ag colloids.¹⁰ Thus the absence of any peak at 850cm^{-1} is an indication that CrO_4^- is not stable on a Ag electrode after an ORC.

The results for H_2O solutions are the same except that the two peaks are barely distinguishable at any V_{SCE} . At $-0.45V_{\text{SCE}}$ during the most favorable conditions of an anodic sweep, the peaks occurred at 573 and 642 cm^{-1} .

Figure 2 shows the effect of periodic addition of O_2 gas at 1 atm pressure to the electrolyte at a distance of 1 cm from the Ag electrode. The cell voltage is maintained at $-1.24V_{\text{SCE}}$ after an initial ORC which removed and redeposited ~ 10 layers of Ag. The first spectral frame shows that the 573 cm^{-1} peak is the most intense under these conditions. The addition of O_2 gas at frame 5 causes the 642 cm^{-1} peak to appear. Stopping the O_2 gas flow in frame 10 causes the 642 cm^{-1} peak to decrease in intensity once again. The process is repeatable as shown in Fig. 2. This result is similar to that obtained for cells where the MnO_4^- was substituted for CrO_4^- . It appears that the 642 cm^{-1} peak is due to an adsorbed oxide layer formed by deprotonation of the adsorbed hydroxide appearing at 573 cm^{-1} .

DISCUSSION

The SERS peaks observed at 642 and 573 cm^{-1} in H_2O are assigned to the stretching modes of the adsorbed species $(\text{Ag,Cr})-\text{O}$ and $(\text{Ag,Cr})-\text{OH}$ where (Ag, Cr) indicates chromium species incorporated into the Ag surface. The assignments are based on the following facts:

1. The 642 cm^{-1} peak occurs at the same frequency shift regardless of the isotopic composition of the solvent. On the other hand the 573 cm^{-1} peak in H_2O is shifted by -7cm^{-1} to 566 cm^{-1} in D_2O . Assuming a harmonic oscillator approximation for $\text{Ag}-\text{OH}$, the calculated shift is -14 cm^{-1} .
2. The behavior of the two SERS peaks after an ORC in CrO_4^- solution is reminiscent of the results previously obtained for MnO_4^- solutions.^{4a} During the cathodic sweep, the in-

terfacial pH decreases due to electrostatic attraction of hydrated H^+ ions.⁶ The (Ag,Cr)-O species are protonated with a simultaneous electron transfer to form (Ag,Cr)-OH. This results in a decrease in the intensity of the 642 cm^{-1} peak and an increase in the 573 cm^{-1} peak. During an anodic sweep, the process is reversed as the hydroxide is deprotonated.

3. The addition of O_2 gas to the electrolyte demonstrates that the two peaks are related chemically. The 573 cm^{-1} peak is generated by the addition of O_2 while the cell voltage and bulk solution pH are such that adsorbed OH^- should be the stable species. As in the case of the MnO_4^- solutions, the oxygen reduction at the cathode according to the overall reaction, $O_2 + 2H_2O + 4e^- = 4OH^-$, increases the interfacial pH and deprotonates the (Ag,Cr)-OH to form (Ag,Cr)-O. Stopping the flow of O_2 decreases the interfacial pH and the oxide is again protonated.

The assignment of the SERS active site is problematic. The only observed SERS spectrum for Ag_2O has been observed on coldly deposited Ag films¹² at $\sim 200\text{--}500\text{ cm}^{-1}$. EELS measurements on Ag(110) give 315 and 630 cm^{-1} for adsorbed oxygen species on Ag.¹³ In strongly basic NaOH solutions, SERS peaks at 490 and 430 cm^{-1} are observed which have been assigned to 'AgO', a mixed valence compound of Ag_2O and Ag_2O_3 .¹⁴ Attempts by several groups to measure ordinary Raman scattering from Ag_2O powders have failed. However, infrared measurements show a fundamental absorption at 545 cm^{-1} . It is clear from these results that the vibrational frequency of oxygen adsorbed on Ag metal lies in the spectral region from ~ 300 to 600 cm^{-1} .

Several of the vibrational modes of chromic oxide and chromic hydroxide derivatives are also expected to occur in this region. The major IR absorptions of Cr_2O_3 due to $K = 0$ phonons occur at 550 and 618 cm^{-1} .¹⁵ IR measurements on various preparations of hydrated Cr_2O_3 powders show a very broad peak centered at 550 cm^{-1} . Anhydrous Cr_2O_3 exhibits two peaks at ~ 565 and 625 cm^{-1} .¹⁶ From these results it is clear that the SERS active site could be a pure Ag ion site, a localized a Cr species, or a site involving both Cr and Ag. Because Cr metal itself is not expected to give rise enhanced Raman scattering,¹⁷

we suggest that the active site is a mixed metal oxide symbolized by (Ag,Cr)-O.

The (Ag,Cr)-O site differs from the (Ag,Mn)-O site in that the hydroxide covered surface cannot be protonated further as a function of V_{SCE} . In contrast, the (Ag,Mn)-O site may be protonated to form adsorbed water and a hydrogen bonded water dimer. It is known that impurity metals in some catalysts drastically modify the chemical product distribution¹⁸. In electrochemical cells, similar effects are observed using SERS. For instance, the substitution of $MgCl_2$ for KCl in electrolytes containing MnO_4^- causes the voltage dependent appearance of adsorbed OH^- rather than adsorbed H_2O .¹⁹ The incorporation of Cr into Ag during an ORC seems to modify the surface potential such that the interfacial pH is never sufficiently low to cause appreciable protonation of the hydroxide to form adsorbed H_2O .

Chromate solutions are commonly used to passivate metals, particularly steels.²⁰ The rate of corrosion of Ag metal is also decreased by treatment with chromate solutions²¹ yet MnO_4^- solutions increase the rate of corrosion. The anticorrosion properties of chromate treated metals apparently stem from the inability of the surface to form adsorbed interfacial H_2O regardless of the potentials present. A surface containing adsorbed H_2O such as that obtained in MnO_4^- solutions may effect a less random transition to the bulk solution than a surface covered with adsorbed O or OH^- . Further SERS experiments using TcO_4^- , an excellent passivating agent, should be a test of this proposal.

CONCLUSIONS

In this paper evidence is presented to support the following conclusions:

1. (Ag,Cr)-O and (Ag,Cr)-OH is formed on a Ag electrode after an ORC of a solution of KCl which contains micromolar quantities of $Na_2Cr_2O_7$.
2. The (Ag,Cr)-O is protonated to form adsorbed hydroxide, (Ag,Cr)-OH as V_{SCE} is swept cathodically. The addition of O_2 gas to the electrolyte deprotonates the hydroxide to form the (Ag,Cr)-O in a reversible process which involves increasing the interfacial pH.
3. The (Ag,Cr)-OH is not further protonated at any obtainable V_{SCE} , indicating

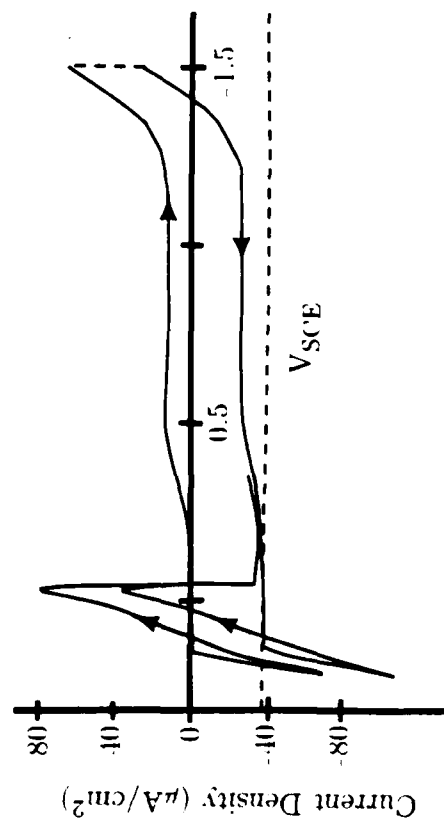
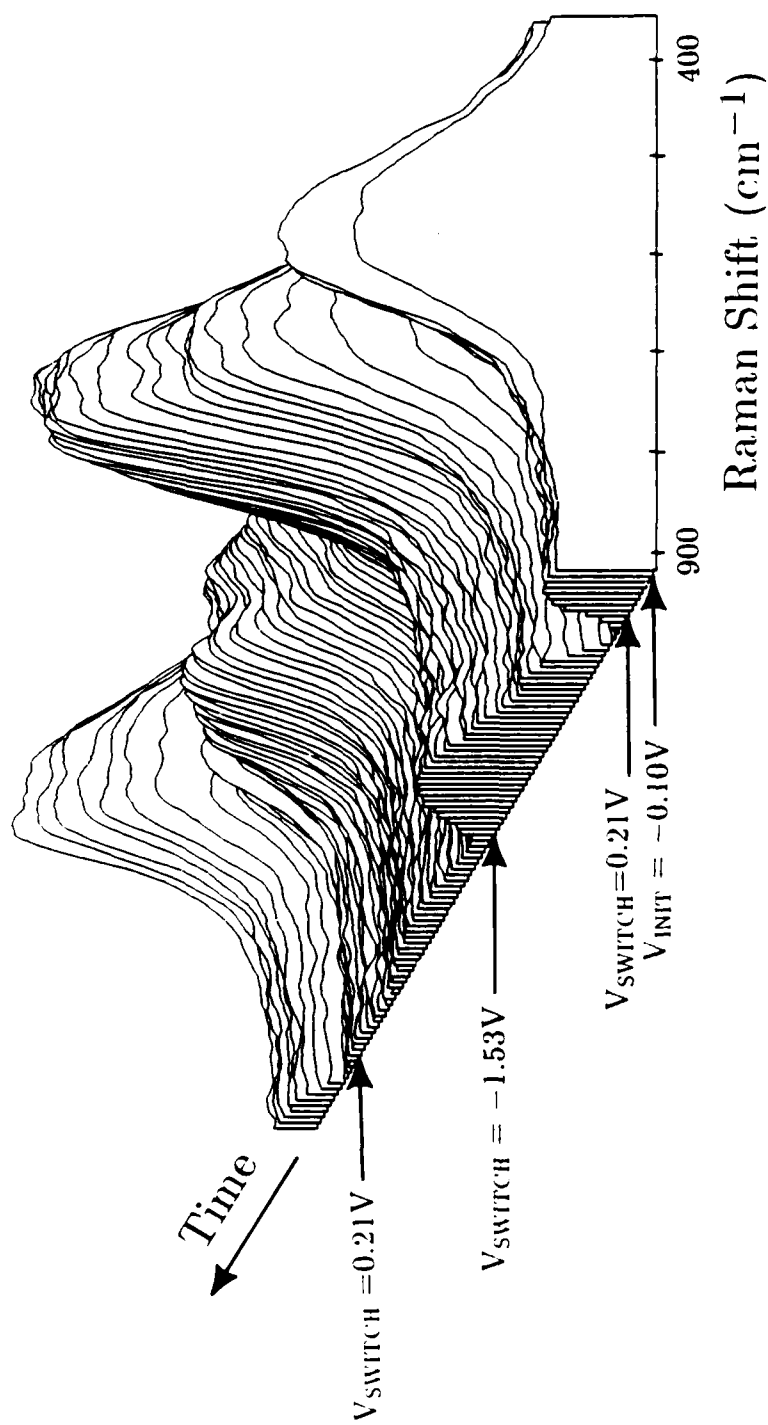
that the surface potential for Ag metal with a $\sim 1\%$ Cr impurity level is strongly modified compared to the case when Cr is replaced with Mn. This difference in the ability of the surface to form SERS active H_2O suggests that the passivation characteristics of CrO_4^- treated metals are related to H_2O -metal interface.

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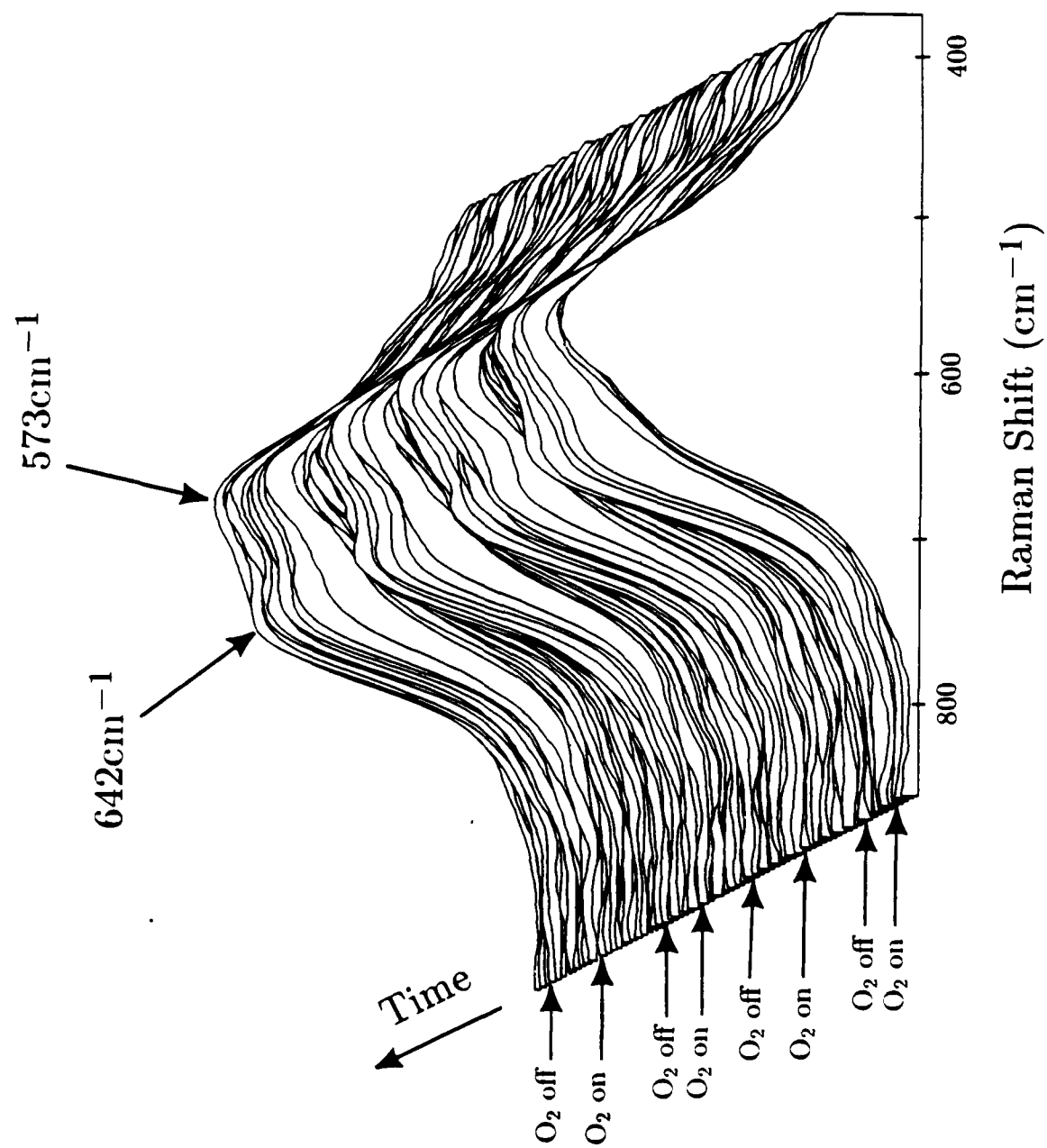


Figure 1. The SERS spectrum from a Ag electrode in a D₂O solution of 50 μ M Na₂Cr₂O₇ and 10⁻²M KCl at a pD of 6.3. The excitation wavelength is 488nm, the laser power is 100mw, and the time interval between frames is 8.7s (43.5mV_{SCE}). A second ORC linear voltage scan begins at frame 2 (-0.10V_{SCE}), sweeping anodically until frame 9 (0.21V_{SCE}), cathodically until frame 49 (-1.53V_{SCE}), anodically again until frame 88 (0.21V_{SCE}), and cathodically again until the end of the experiment.

Figure 2. The SERS spectrum from a Ag electrode in a D₂O solution of 50 μ M Na₂Cr₂O₇ and 10⁻²M KCl at a pD of 6.3. The excitation wavelength is 488nm, the laser power is 100mw, and the time interval between frames is 2.7s. The cell voltage is held constant at -1.24V_{SCE} after an initial ORC. O₂ gas is bubbled through the solution from frames 5 to 10, 22 to 32, 42 to 50, and 62 to 72.

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